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(71) Applicant ( <i>for all designated States except US</i> ): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).			
(72) Inventors; and			
(75) Inventors/Applicants ( <i>for US only</i> ): MALLANT, Ronald, Karel, Antoine, Maria [NL/NL]; Koggewaard 83, NL-1824 GP Alkmaar (NL). CALIS, Gijsbertus, Hendrikus, Maria [NL/NL]; Burg. Kengenstraat 60, NL-6336 BK Nuth (NL). DE BRUIJN, Frank, Albert [NL/NL]; Canneburg 23, NL-1823 HP Alkmaar (NL).			
(74) Agent: MOOIJ, Johannes, Jacobus; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).			
(54) Title: ELECTROLYTIC MEMBRANE, METHOD OF MANUFACTURING IT AND USE			
(57) Abstract			
<p>Electrolytic membrane comprising an ion-conducting polymer which is fixed in the pores of a porous polyalkene membrane stretched in at least one direction, wherein the polyalkene membrane has a porosity of 30-90 % and a mean pore diameter of 0.1 to 5.0 <math>\mu\text{m}</math>. The electrolytic membrane can be manufactured by impregnating the polyalkene with a suitable solution of the ion-conducting polymer at a temperature which is at least 80 <math>^{\circ}\text{C}</math>, preferably at least 110 <math>^{\circ}\text{C}</math>, and which is not above the melting point of the polyalkene membrane used. The electrolytic membrane is very suitable for use in solid-polymer fuel cells and batteries.</p>			

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ELECTROLYTIC MEMBRANE, METHOD OF MANUFACTURING IT  
AND USE

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The invention relates to an electrolytic membrane comprising an ion-conducting polymer which is fixed in pores of a polyalkene membrane whose porosity 10 is 30-90% by volume. Such membranes are used, for example, in fuel cells, electrolysis cells, primary and secondary batteries. In particular, such membranes are used at points where a high ion conductivity is desired in combination with a high mechanical strength.

15 Although a high ion conductivity can be obtained by using a membrane having a small thickness, a small thickness is generally achieved at the expense of the strength of the membrane.

Such membranes are disclosed in US-A-20 4,849,311. US-A-4,849,311 describes an electrolytic membrane which contains an ion-conducting polymer which is fixed in the pores of a porous polyethylene membrane. The porosity of the membrane described in US-A-4,865,930. is between 40 and 90%. The pores have a 25 mean size between 0.001  $\mu\text{m}$  and 0.1  $\mu\text{m}$ . According to the teaching of US-A-4,849,311, pores having a mean diameter greater than 0.1  $\mu\text{m}$  are difficult to fill and, once filled, the electrolyte easily leaks out again. The membrane is preferably made of polyethylene having 30 a weight-average molar mass of at least 500,000 g/mol. Nafion<sup>®</sup> is described as ion-conducting polymer; a perfluorocarbon compound containing a sulphonic acid group.

A disadvantage of such a membrane is that the 35 ion conductivity is relatively low.

The object of the invention is to provide an electrolytic membrane having a higher ion conductivity.

According to the invention, this object is achieved in that the membrane is stretched in at least

one direction and has a mean pore size between 0.1 and 5  $\mu\text{m}$ .

5 The membrane according to the invention is found to have a higher ion conductivity than a known membrane having a smaller pore size and a comparable membrane thickness, porosity and strength.

10 An advantage of the membrane according to the invention is that it is gastight, as a result of which the membrane is very suitable to be used in a solid-polymer fuel cell.

15 The membrane according to the invention contains an ion-conducting polymer. Ion-conducting polymers which can be used are known and a few are even commercially available. Suitable polymers are described in Patent Specifications US-A-4,849,311 and US-A-4,865,930. Ion-conducting polymers which are preferably used are polymers based on perfluorosulphonic acid and copolymers of tetrafluoroethylene with perfluorosulphonyl ethoxyvinyl ether are very suitable, 20 the sulphonyl groups being converted into sulphonic acid groups. Such polymers are commercially available under the brand names Nafion and Aciplex. Other examples of suitable ion-conducting polymers are complexes of alkali-metal or alkaline-earth-metal salts 25 with a polar polymer. Examples of these are polyethylene glycol ethers. Complexes of the abovementioned polymers with an ion-donating acid can also be used.

30 In the membrane according to the invention, the ion-conducting polymer is fixed in the pores of a polyalkene membrane.

35 Suitable as porous polyalkene membrane are, in particular, porous membranes of polyethylene, polypropylene and ethylene-propylene copolymers. The porosity of the polyalkene membrane according to the invention is between 30 and 90% by volume. This means that the volume of the pores accounts for 30-90% by

volume of the total volume of the total membrane.

It has been found that, at a porosity lower than 30%, the ion conductivity of the membrane decreases, while, at a porosity greater than 90%, the 5 mechanical strength decreases undesirably.

The best results are obtained with a polyalkene membrane having a porosity of 60 to 85%.

The membrane according to the invention is stretched in at least one direction and has a mean pore 10 size between 0.1 and 5  $\mu\text{m}$ . In J. Electroanal. Chem. 235 (1987), 299-315, J. Leddy and N. E. Vanderborgh describe how the transport through a Nafion phase, and therefore also the ion conductivity, decreases at pore diameters greater than 0.05  $\mu\text{m}$ . Surprisingly it was 15 found that, indeed, a membrane stretched in at least one direction having a pore diameter greater than 0.05  $\mu\text{m}$  has a better ion conductivity than a membrane having a pore diameter smaller than 0.05  $\mu\text{m}$ .

With a mean pore diameter greater than 5.0 20  $\mu\text{m}$ , the ion-conducting polymer can no longer be fixed in the pores because the pores are then too large. The best results are obtained with a pore diameter of 0.15 to 2.5  $\mu\text{m}$ .

The electrolytic membrane according to the 25 invention has a good mechanical strength, as a result of which no cracks occur even in the case of relatively thin membranes if the membrane is processed for its application. The electrolytic membrane according to the invention preferably has a tensile strength of at least 30 15 MPa, while the thickness of the membrane may vary from 15 to 150  $\mu\text{m}$ , preferably from 20 to 60  $\mu\text{m}$ . With such a thickness, the membrane according to the invention has an ion conductivity of at least 0.0004 S/cm, but the ion conductivity is preferably 35 considerably higher, i.e. at least 0.0008 S/cm, while a particularly suitable membrane has an ion conductivity of 0.002 to 0.08 S/cm.

The invention also relates to a method of manufacturing the electrolytic membrane according to the invention.

Such a method is disclosed in US-A-4,849,311.

5 In it, the pores of a porous membrane, preferably polyalkene membrane, are filled by means of capillary condensation with a solution of an ion-conducting polymer.

A disadvantage of the method described in US-10 A-4,849,311 is that it is difficult to manufacture an electrolytic polyalkene membrane whose pores have a mean diameter of more than 0.1  $\mu\text{m}$ . According to the said patent specification, the mean pore diameter should preferably be even less than 0.025  $\mu\text{m}$ . The 15 reason given for this is that the ion-conducting polymer leaks away from pores greater than 0.1  $\mu\text{m}$  so that such a membrane is unstable.

The object of the invention is to eliminate said disadvantage completely or partially.

20 According to the invention said object is achieved by a method which comprises the following steps:

a) dissolving an ion-conducting polymer in a solvent, at least 25% by weight of which is composed of a 25 component having a boiling point higher than 125°C,

b) applying an amount of the solution prepared under (a) to a horizontal polyalkene membrane stretched in at least one direction and having a pore volume 30 of 30-90% of the total volume of the membrane, the amount of the solution being chosen in such a way that the volume of the ion-conducting polymer present therein is more than 60% of the pore volume, and the membrane being sealed at the 35 underside,

c) evaporating the solvent at a temperature which is at least 80°C and which is lower than the melting

point of the polyalkene membrane.

5 A stable electrolytic membrane having an ion-conducting polymer fixed in the pores of a polyalkene membrane having a mean pore size between 0.1 and 5.0  $\mu\text{m}$  is manufactured by the method according to the invention.

10 An advantage of the method according to the invention is that the ion-conducting polymer which is present in the solution on the horizontal stretched membrane becomes preferentially concentrated at the polyalkene surface. Since most of the surface is in the pores, the ion-conducting polymer becomes concentrated in the pores of the membrane. A method in which 15 partially filled pores need to be refilled with a fresh solution can thereby be avoided. The disadvantage of refilling pores is that air inclusions are easily produced. The refilling of partially filled pores is therefore only possible in the presence of solvents, which have a low wetting angle with the polyalkene. 20 Such a limitation does not apply in the case of the method according to the invention.

25 A further advantage of the method according to the invention is that a porous membrane having a pore size above 0.1  $\mu\text{m}$  is easy to impregnate, as a result of which virtually no air is enclosed in the membrane.

30 In the method according to the invention, an ion-conducting polymer is dissolved in a solvent, at least 25% by weight of which is composed of a component having a boiling point higher than 125°C. Solutions of 35 ion-conducting polymers can be prepared as described in, for example, US-A-4,849,311. A good method of obtaining a suitable solution of an ion-conducting polymer is, for example, heating the solid polymer in a suitable solvent. Suitable solvents for the preferred polymers perfluorosulphonic acid-based polymers are water and alcohols such as ethanol, n-propanol or

isopropanol. The presence of a component having a boiling point of more than 125°C ensures that the evaporation takes place slowly. This, in combination with a particular pore structure of a stretched membrane, results in the ion-conducting polymer no longer, or scarcely any longer, dissolving after the solvent has evaporated. As a result, a stable membrane is obtained. Suitable components having a boiling point of more than 125°C are, for example, ethylene glycol, 10 N,N-dimethylformamide and dimethyl sulphoxide.

Preferably, the component having a boiling point higher than 125°C in the solvent and the amount thereof are chosen in such a way that the evaporation takes between 10 and 24 hours.

15 Preferably, at least 50% by weight of the solvent is composed of a component having a boiling point higher than 150°C. This ensures that the evaporation can take place at a higher temperature without the evaporation time being substantially shortened as a consequence. A further advantage of a 20 component having a boiling point higher than 150°C is that less of it is necessary to arrive at the desired evaporation time than of a solvent having a lower boiling point. Consequently, the choice of solvent is 25 less critical. In particular, if more than 50% by weight of the component having a boiling point higher than 150°C is present, higher requirements are imposed on the solubility of the ion-conducting polymer in said component than if said percentage is significantly 30 below 50% by weight. Preferably, the component having a boiling point higher than 150°C is dimethyl sulphoxide (DMSO). The advantage of DMSO is that it has a boiling point of 189°C and is not toxic.

35 A suitable concentration of the ion-conducting polymer in the solvent is between 2 and 25% by weight. Preferably, a solution is used in which the concentration of ion-conducting polymer is 2-5% by

weight.

It has been found that slow evaporation at a temperature which is as little as possible below the melting point of the polyalkene membrane adds to the 5 insolubility of the solid ion-conducting polymer formed in the pores.

In the method according to the invention, an amount of the abovementioned solution is applied to a horizontal polyalkene membrane stretched in at least 10 one direction and having a pore volume of 30-90% of the total volume of the membrane, the amount of the said solution being chosen so that the volume of the ion-conducting polymer present therein is more than 60% of the pore volume and the membrane being sealed at the 15 underside.

This ensures that, after the evaporation of the solvent, at least nearly 60% by volume of the pores are filled with the ion-conducting polymer. The fact that a small portion of the ion-conducting polymer 20 remains behind on the surface of the membrane has the result that the amount of ion-conducting polymer in the pores is somewhat below the amount calculated on the basis of the pore volume. Preferably, the amount of the solution is chosen in such a way that at least 80% by 25 volume, or still more preferably, at least 95% by volume of the pores are filled with the ion-conducting polymer. Since, as described above, the ion-conducting polymer preferentially deposits on the polyalkene surface and the total pore surface is many times 30 greater than the outer surfaces of the membrane, the ion-conducting polymer which deposits on the outer surface of the membrane can be neglected in the calculation of the amount of solution containing ion-conducting polymer.

35 A measure for facilitating the impregnation is first to wet the membrane with the solvent prior to impregnating it with the solution of the ion-conducting

polymer.

Polyalkene membranes which are stretched in at least one direction are disclosed in EP-A-504,954. EP-A-504,954 describes a method of preparing a 5 polyalkene membrane from a solution of a polyalkene in a volatile solvent. The membrane passes through a cooling bath containing a coolant and the solvent is removed at a temperature below the temperature at which the polyalkene dissolves in the solvent, after which 10 the membrane is stretched in at least one direction. If the polyalkene is polyethylene, the weight-average molecular weight may vary between 100,000 and 5,000,000 g/mol. Preferably, the membrane contains polyethylene having a weight-average molecular weight which is less 15 than 500,000 g/mol. It has been found that, in the presence of polyethylene having such a molecular weight, it is easy to manufacture membranes having a mean pore size between 0.1 and 5.0  $\mu\text{m}$ . Suitable, in particular, are mixtures of polyethylene with various 20 molecular weights. Thus, a mixture which contains polyethylene having a weight-average molecular weight less than 500,000 g/cm<sup>3</sup> can also contain polyethylene having a weight-average molecular weight greater than 1,000,000 g/cm<sup>3</sup>. As a result of the presence of the 25 latter polyethylene, a high strength of the membrane is obtained.

During the application of the solution of the ion-conducting polymer, the membrane is sealed at the underside. This prevents the solution applied to the 30 membrane from leaving the membrane at the underside and thus from being lost for deposition in the pores of the membrane. The sealing of the membrane at the underside can be effected by, for example, clamping the membrane onto a flat plate.

35 The solution applied to the membrane is then evaporated at a temperature which is at least 80°C and which is lower than the melting point of the polyalkene

membrane. Preferably, the temperature at which the solvent is evaporated is more than 110°C, the evaporation time being, as already described above, at least 10 hours. It has been found that the higher the 5 temperature at which evaporation is carried out, the lower is the solubility of the solid ion-conducting polymer formed in the H<sup>+</sup> form.

Before using the membrane according to the invention, for example in a solid-polymer fuel cell, it 10 should be cleaned. This is possible in various ways and the way in which it is done is not essential for the invention. Any known cleaning procedure can therefore be used. Successive or alternating cleaning with water (Millipore-filtered, 18 megaohm·cm, ultrasound), 15 hydrogen peroxide solution and sulphuric acid solution is a very suitable method.

The electrolytic membranes according to the invention are very suitable for use in fuel cells and, in particular, in solid-polymer fuel cells or polymer-electrolyte fuel cells. Such fuel cells are known per 20 se. Another use of the electrolytic membrane according to the invention is in batteries. The invention also relates to fuel cells and batteries in which the electrolytic membrane is used.

25 A solid-polymer fuel cell comprises a porous platinum anode and a porous platinum cathode which are both in contact with the electrolytic membrane. In the standard H<sub>2</sub>/O<sub>2</sub> polymer fuel cell, H<sub>2</sub> is oxidized at the anode to H<sup>+</sup> ions which are transported through the 30 membrane to the cathode. Water is then formed at the cathode by reduction of O<sub>2</sub> in the presence of H<sup>+</sup>. As a result of the electroosmotic effect, at the anode, water is likewise removed together with H<sup>+</sup> through the membrane to the cathode. As a result, there is a risk 35 that drying-out of the anode will occur. In order to combat such drying-out of the membrane, the reactant gases are moistened. A solid-polymer fuel cell is

usually operated at a temperature of around 80°C.

The invention is further illustrated by reference to the examples below.

5 Example I

2.8 g of a 5% Nafion 1100 solution in the H<sup>+</sup> form (Solution Technology) is mixed with 2.16 g of dimethyl sulphoxide. The impregnation was carried out by applying said solution to a porous polyethylene 10 membrane stretched in two directions (5 x 5) (Solupor<sup>®</sup> type 7P20 from DSM Solutech B.V.) having a surface area of 25 cm<sup>2</sup>, a thickness of 40 µm and a porosity of 81%. The weight-average molecular weight of the polyethylene was  $4.5 \times 10^5$  g/mol and the mean pore diameter was 2.0 15 µm. The membrane was clamped onto a flat 316L stainless-steel plate. Directly afterwards, the membrane with the impregnation solution on it was placed in an oven where it was heated slowly to 126°C at atmospheric pressure. The evaporation time was 16 20 hours.

After the impregnation was complete, it was found that 100% of the pore volume of the membrane was occupied by Nafion 1100. The density of the Nafion in the pores was 1.56 g/cm<sup>3</sup>.

25

Example II

The impregnated membrane from Example I was then tested in a solid-polymer fuel cell. For this purpose, it was first cleaned by successively cleaning 30 it ultrasonically in 18 megaohm·cm Millipore-filtered water, allowing it to stand for 60 minutes in 3% hydrogen peroxide at 100°C, again cleaning it ultrasonically in 18 megaohm·cm Millipore-filtered water, allowing it to stand for 60 minutes in 1 M 35 sulphuric acid at 80°C and, finally, cleaning it again ultrasonically in 18 megaohm·cm Millipore-filtered water.

Both sides of the membrane were then coated with 0.1 gramme of an ink composed of 52% 1-propanol, 8% of a 20% by weight Pt/Vulcan catalyst (Vulcan is the trade name of an active carbon having a BET surface area of approximately 300 m<sup>2</sup>/g) and 40% of the 5% by weight Nafion 1100 solution from Solution Technology. The Pt loading was consequently 0.2 mg/cm<sup>2</sup> of cell surface.

The test conditions were as follows:

10	Type of fuel/oxidant	H <sub>2</sub> /air
	Pressure	3 bar
	Type of flow	co-current flow
	Load	0.5 V
	Air moistening temperature	85°C
15	H <sub>2</sub> moistening temperature	90°C
	H <sub>2</sub> /air stoichiometry	1.5/2.5
	Cell temperature	80°C

The measured open-circuit voltage of the fuel cell was 0.918 V and the conductivity of the membrane 20 was at least 0.023 S/cm.

Figure 1 shows the polarization curve of the fuel cell.

### Example III

25 A polyethylene membrane (Solupor Type 7P20) stretched in two directions (5 x 5) and having a surface area of 25 cm<sup>2</sup>, a thickness of 40 µm, a porosity of 81% and a mean pore diameter of 1.5 µm was clamped in a stainless-steel jig shown in Figure 2 and was 30 first wetted with 3 grammes of dimethyl sulphoxide and then impregnated with 4 grammes of a solution which contained 5% Nafion (1100). The jig was then placed in an oven at a temperature of 126°C. After 16 hours, the jig was taken out of the oven and water was poured over 35 the membrane in order to facilitate release from the jig. The thickness of the membrane determined with the aid of a Mitutoyo Digimatic Indicator ID 110M was 51.1

μm. The membrane was then placed in a beaker and 10 ml of sodium chloride (1 mol/l) was poured over it. The Nafion content was determined by means of an acid-base titration with the aid of phenolphthalein. The density of the Nafion was determined from a film cast from the solution which had undergone the same drying as the membrane. The density of the Nafion was 1.56 g/cm<sup>3</sup>. The Nafion content determined by means of acid-base titration was found to be 100% by volume of the pore 10 volume of the Solupor membrane.

Example IV

A polyethylene membrane (Solupor 7P03) stretched in two directions (5 × 5) and having a 15 surface area of 25 cm<sup>2</sup>, a thickness of 35 μm, a porosity of 78% and a mean pore diameter of 0.3 μm was clamped in a stainless-steel jig as shown in Figure 2 and was first wetted with 1.9 grammes of dimethyl sulphoxide and then impregnated with 2.5 grammes of a solution 20 which contained 5% Nafion (1100). The jig was then placed in an oven at a temperature of 124°C. After 16 hours, the jig was taken out of the oven and water was poured over the membrane in order to facilitate release from the jig. The thickness of the membrane determined 25 with the aid of a Mitutoyo Digimatic Indictor ID 110M was 25.6 μm. The Nafion content was found to be 100% by volume of the original pore volume of the Solupor membrane.

30 Example V

A polyethylene membrane (Solupor type 7P03) having a surface area of 25 cm<sup>2</sup>, a thickness of 35 μm, a porosity of 78% and a mean pore diameter of 0.3 μm was clamped in a stainless-steel jig as shown in Figure 2 35 and was first wetted with 1.9 grammes of dimethyl sulphoxide and then impregnated with 2.5 grammes of a solution which contained 5% Aciplex having an

equivalent weight of 950 g/mol (Asahi Chemical). The jig was then placed in an oven at a temperature of 126°C. After 16 hours, the jig was taken out of the oven and water was poured over the membrane in order to 5 facilitate release from the jig.

The thickness of the membrane determined with the aid of a Mitu Toyo Digimatic Indicator ID 110M was 29.7  $\mu\text{m}$ .

10 The Nafion content was found to be 100% by volume of the original pore volume of the Solupor membrane.

#### Example VI

15 The membrane of Example III was successively cleaned in a 3% peroxide solution, Millipore-filtered 18 megaohm·cm water, 1 M sulphuric acid and Millipore-filtered 18 megaohm·cm water. Two platinum-on-carbon gas-diffusion electrodes (E-TEK Inc.) having a surface area of 6.76  $\text{cm}^2$  and having a platinum content of 0.35 20 mg/ $\text{cm}^2$  were hot-pressed onto both sides of said membrane and served as anode and cathode of a solid-polymer fuel cell. This membrane-electrode assembly was tested as a solid-polymer fuel cell at a cell temperature of 80°C with hydrogen as fuel and air as oxidant, both at a gas 25 pressure of 3 bar absolute. The hydrogen gas was moistened at 90°C and the air was moistened at 60°C. Figure 3 shows the current density at 0.5 V as a function of time. The polarization curve of the cell is presented in Figure 4.

30

#### Example VII

35 The membrane of Example III was successively cleaned in a 3% peroxide solution, Millipore-filtered 18 megaohm·cm water, 1 M sulphuric acid and Millipore-filtered 18 megaohm·cm water. 0.1 g of a 40% platinum-on-carbon catalyst paste was applied to both sides of said membrane. After evaporation of the paste solvent

at ambient temperature, both an anode and a cathode having a platinum content of 0.3 mg/cm<sup>2</sup> were obtained. This membrane-electrode assembly was tested as a solid-polymer fuel cell at a cell temperature of 80°C with 5 hydrogen as fuel and air as oxidant, both at a gas pressure of 3 bar absolute. The hydrogen gas was moistened at 90°C and the air was moistened at 60°C. Figure 5 shows the current density at 0.5 V as a function of time. The polarization curve of the cell is 10 presented in Figure 6. From the comparison of the results of Examples VI and VII it is evident that the electrodes formed with paste are a good alternative to the hot-pressed electrodes.

15 Example VIII

The membrane of Example V was successively cleaned in a 3% peroxide solution, Millipore-filtered 18 megaohm·cm water, 1 M sulphuric acid and Millipore-filtered 18 megaohm·cm water. Two platinum-on-carbon 20 gas-diffusion electrodes having a surface area of 6.76 cm<sup>2</sup> and a platinum content of 0.35 mg/cm<sup>2</sup> (E-TEK Inc.) were hot-pressed onto both sides of said membrane and served as anode and cathode of a solid-polymer fuel cell. This membrane-electrode assembly was tested in a 25 solid-polymer fuel cell at a cell temperature of 80°C with hydrogen as fuel and air as oxidant, both at a gas pressure of 3 bar absolute. The hydrogen gas was moistened at 90°C and the air was moistened at 60°C. Figure 7 shows the current density as a function of 30 time at a cell voltage of 0.6 V. After 48 hours, the current density was found to be 0.777 A/cm<sup>2</sup>, while the current density after 3000 hours was still 0.812 A/cm<sup>2</sup>. If the original current density is defined as the 35 current density after 48 hours, it is evident from this that the current density after 3000 hours through a membrane according to the invention provided with platinum-on-carbon electrodes as a solid-polymer fuel

cell is at least 90% of the original current density at 0.6 V. The polarization curve of the cell is presented in Figure 8.

5 Example IX

A polyethylene membrane (Solupor type 7P03) having a surface area of 300 cm<sup>2</sup>, a thickness of 35 µm, a porosity of 78% and a mean pore diameter of 0.3 µm was completely moistened with dimethyl sulphoxide and 10 then clamped in a stainless-steel jig as shown in Figure 2 and impregnated with a mixture of 27 grammes of dimethyl sulphoxide and 35.5 grammes of a solution which contained 5% Nafion 1100. The jig was then placed in an oven at a temperature of 112°C. After 16 hours, 15 the jig was taken out of the oven and water was poured over the membrane in order to facilitate release from the jig.

The thickness of the membrane determined with the aid of a Mitutoyo Digimatic Indicator ID 110M was 20 between 37 and 48 µm.

Example X

A surface area of 100 cm<sup>2</sup> of the membrane of Example IX was successively cleaned in a 3% peroxide 25 solution, Millipore-filtered 18 megaohm·cm water, 1 M sulphuric acid and Millipore-filtered 18 megaohm·cm water. Two platinum-on-carbon gas-diffusion electrodes having a surface area of 50 cm<sup>2</sup> and a platinum loading of 0.35 mg/cm<sup>2</sup> (E-TEK Inc.) were hot-pressed onto both 30 sides of said membrane and served as anode and cathode of the solid-polymer fuel cell. This membrane-electrode assembly was tested as a solid-polymer fuel cell at a cell temperature of 80°C with hydrogen as fuel and air as oxidant, both at a gas pressure of 3 bar absolute. 35 The hydrogen gas was moistened at 90°C and the air was moistened at 60°C. Figure 9 shows the current density as a function of time at a cell voltage of 0.5 V. The

polarization curve of the cell is presented in Figure 10. From this it is evident that the polarization curve and the stability of the current density are not influenced by the size of the membrane surface.

C L A I M S

1. Electrolytic membrane comprising an ion-conducting polymer which is fixed in pores of a polyalkene membrane whose porosity is 30-90% by volume, characterized in that the membrane is stretched in at least one direction and has a mean pore size between 0.1 and 5  $\mu\text{m}$ .
- 10 2. Electrolytic membrane according to Claim 1, in which the ion-conducting polymer is a polymer based on perfluorosulphonic acid, preferably a copolymer of tetrafluoroethylene with perfluorosulphonyl ethoxyvinyl ether, wherein the 15 sulphonyl groups are converted into sulphonic acid groups.
3. Electrolytic membrane according to Claim 1 or 2, in which the polyalkene is polyethylene.
4. Electrolytic membrane according to one or more of 20 Claims 1-3, in which the mean pore diameter of the polyalkene membrane is 0.15 to 2.5  $\mu\text{m}$ .
5. Electrolytic membrane according to one or more of Claims 1-4, in which said membrane has a thickness of 15 to 150  $\mu\text{m}$ , preferably 20 to 60  $\mu\text{m}$  and an ion 25 conductivity of at least 0.0004 S/cm, preferably at least 0.0008 S/cm.
6. Method of manufacturing an electrolytic membrane according to one of Claims 1-5, which comprises the following steps:
  - 30 a) dissolving an ion-conducting polymer in a solvent, at least 25% by weight of which is composed of a component having a boiling point higher than 125°C,
  - b) applying an amount of the solution prepared 35 under (a) to a horizontal polyalkene membrane stretched in at least one direction and having a pore volume of 30-90% of the total

volume of the membrane, the amount of the solution being chosen in such a way that the volume of the ion-conducting polymer present therein is more than 60% of the pore volume, and the membrane being sealed at the underside,

5 c) evaporating the solvent at a temperature which is at least 80°C and which is lower than the melting point of the polyalkene membrane..

10 7. Method according to Claim 6, wherein at least 50% by weight of the solvent is composed of a component having a boiling point higher than 150°C.

15 8. Method according to Claim 7, wherein the component having a boiling point higher than 150°C is dimethyl sulphoxide.

9. Method according to one of Claims 6-8, wherein the solvent evaporates at a temperature of at least 20 110°C.

10. Method according to one of Claims 6-9, wherein the polyalkene contains polyethylene having a weight-average molecular weight of less than 500,000 g/mol.

25 11. Use of an electrolytic membrane according to one or more of Claims 1-5 in a fuel cell or battery.

12. Fuel cell or battery which contains an electrolytic membrane according to one or more of Claims 1-5.

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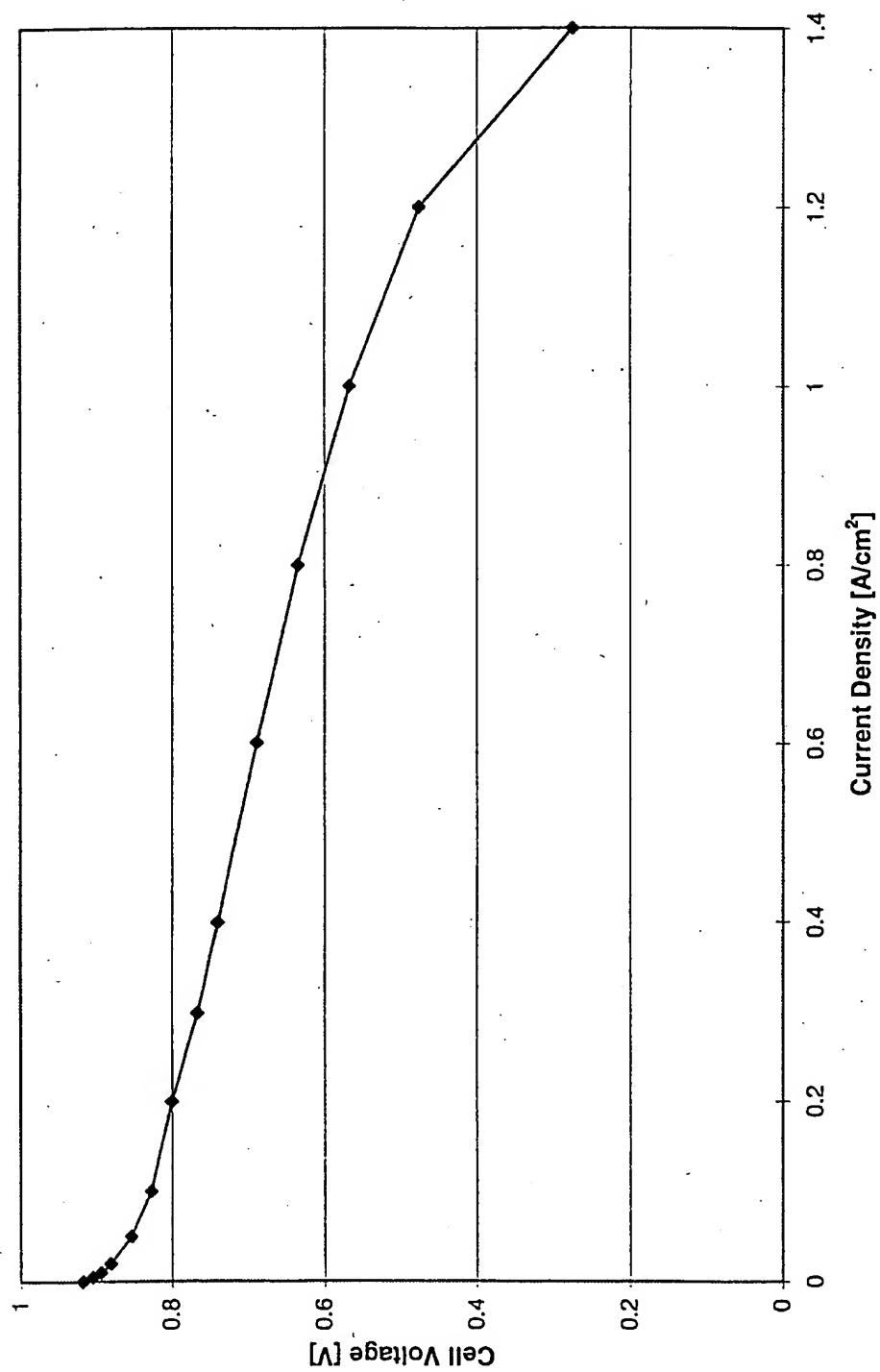


FIG. 1

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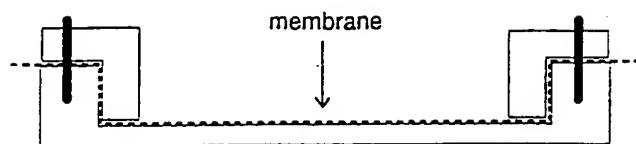


FIG. 2

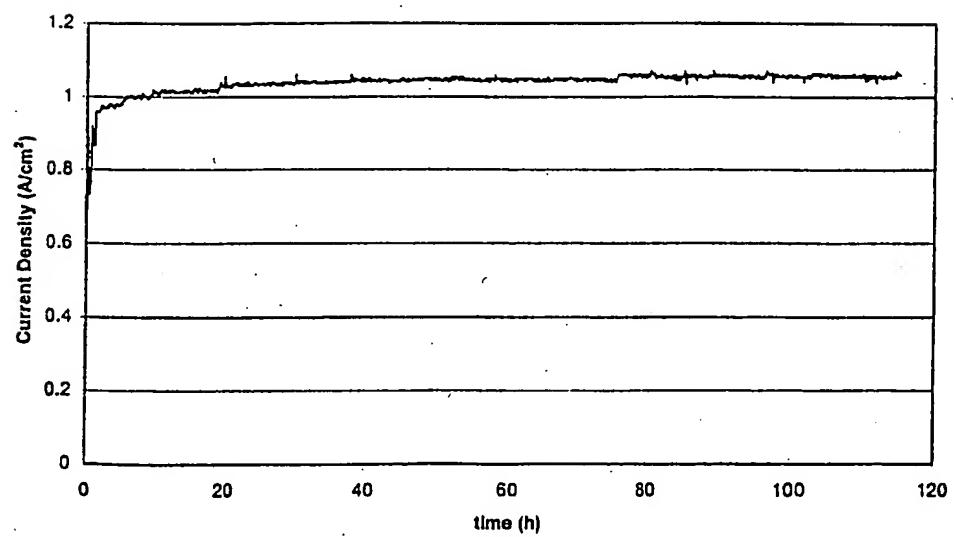


FIG. 3

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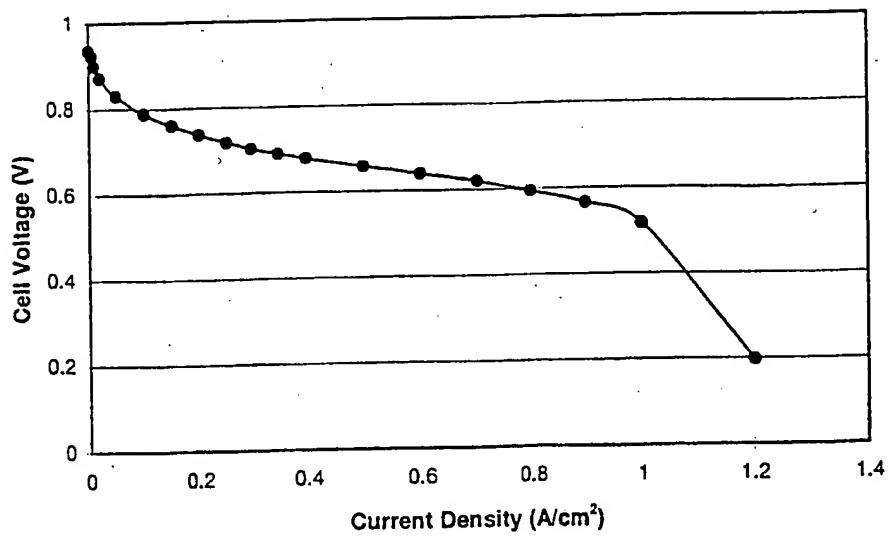


FIG. 4

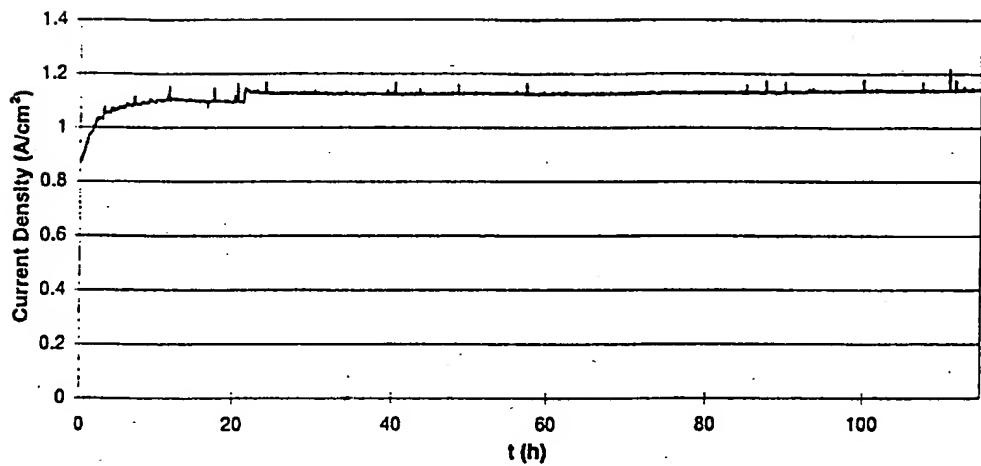


FIG. 5

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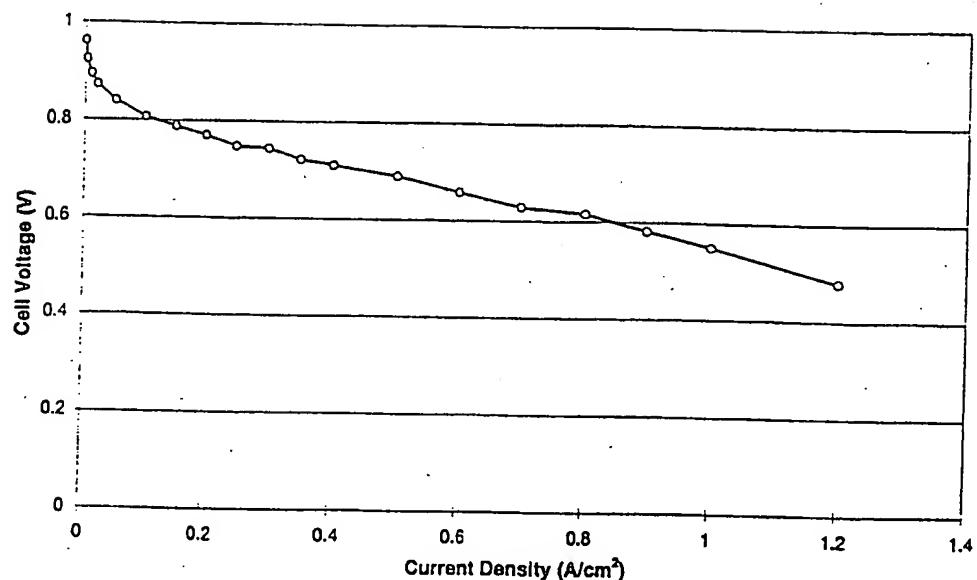


FIG. 6

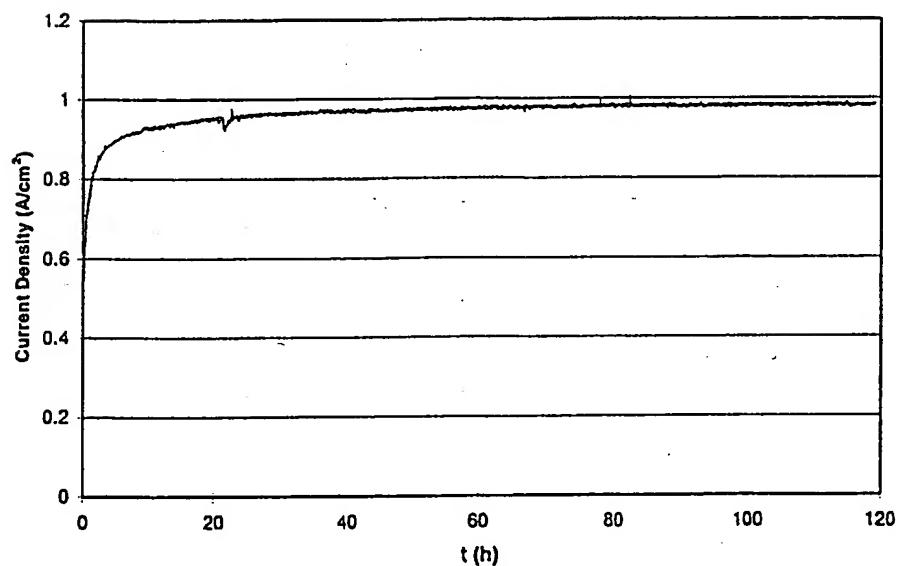


FIG. 7

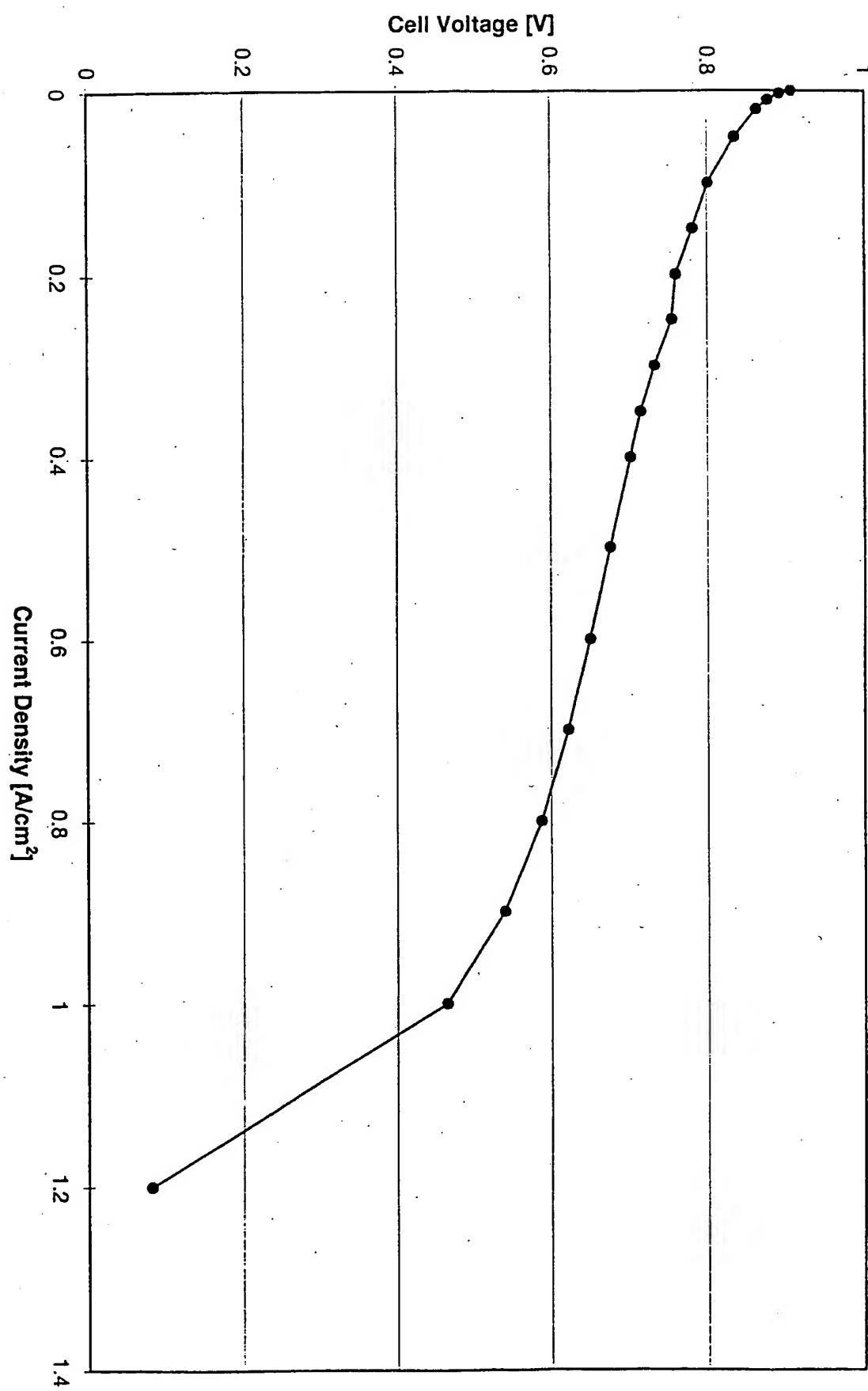


FIG. 8

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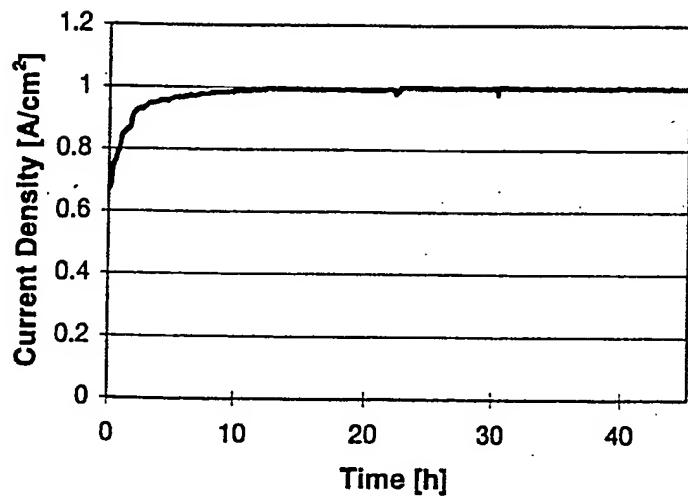


FIG. 9

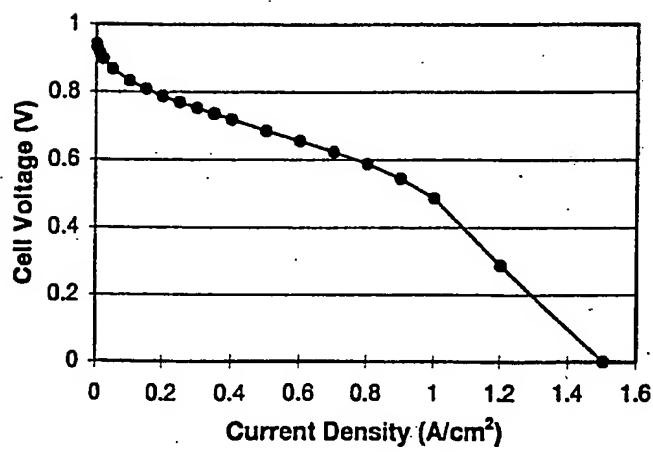


FIG. 10

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 97/00609

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 6 C08J5/22

According to International Patent Classification(IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 309 259 A (TOA NENRYO KOGYO KK) 29 March 1989 see the whole document & US 4 849 311 A cited in the application ---	1-12
Y	DATABASE WPI Section Ch, Week 9509 Derwent Publications Ltd., London, GB; Class A85, AN 95-064423 XP002050614 & JP 06 342 667 A (ASAHI KASEI KOGYO KK) , 13 December 1994 see abstract ---	1-12
Y	EP 0 504 954 A (DSM NV) 23 September 1992 cited in the application see the whole document ---	1-12

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

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- "O" document referring to an oral disclosure, use, exhibition or other means
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1	Date of the actual completion of the international search  3 February 1998	Date of mailing of the international search report  18/02/1998
	Name and mailing address of the ISA  European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl Fax: (+31-70) 340-3016	Authorized officer  Tarrida Torrell, J

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 97/00609

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 326 632 A (DOW CHEMICAL CO) 9 August 1989 see the whole document -----	1-12

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# INTERNATIONAL SEARCH REPORT

## Information on patent family members

International Application No

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